

CORRECTION OF THE DYNAMIC RESPONSE OF OXYGEN PROBE FOR MEASUREMENT OF KINETIC PARAMETERS OF FAST PROCESSES BY DYNAMIC METHODS. COMPARATIVE STUDY

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Existing models, empirical and rational, are compared as to their ability to describe the dynamics of the probes proper, *i.e.* their response to a step change in oxygen concentration. Models are selected describing adequately the behaviour of all available types of probes even under the conditions characterized by a significant resistance in the liquid film adjacent to the membrane of the probe. Relations are derived for the evaluation of the response of the probes applicable to the measurement of the volumetrical mass transfer coefficient ($k_L a$) by dynamic methods in bubble reactors and packed absorption columns with eventual presence of certain types of chemical reactions. These relations apply also to the determination of the reaction rate constant of a first-order reaction in closed reactors. Effects are discussed of the interaction of the probe with bubbles, of the transient period during start-up of aeration and mixing in bubble reactor as well as of the error incurred in ($k_L a$) stemming from incorrect models of the dynamics of the probe itself.

Oxygen probe is a modern analytical instrument, which in connection with the dynamic methods of measurement of transient characteristics of absorption equipment or reaction kinetic constants, represents a powerful scientific tool.

Dynamic method are based on observation of the exponential concentration change following the start-up of a process described by a first order kinetic equation. (*E.g.*: measurement of volumetrical mass transfer coefficient ($k_L a$) in aerated tanks¹ or absorption columns²). Methods of data evaluation utilize models of the mechanisms that become effective during mass transfer toward the probe: the signal of the probe is proportional to mass flux of oxygen toward the cathode. The mass flux is controlled by the resistances offered to mass transfer in the following regions: liquid film adjacent to the membrane, membrane, electrolyte and cathode reaction (Fig. 1). Commonly it is assumed that the electrode reaction is sufficiently fast and its resistance may be neglected. The remaining resistances govern the dynamics of the probe proper which can be evaluated from the response of the probe to an experimentally well-defined signal, most often the concentration step change. The aim of many

papers has been to comprehend the dynamics of the probe to an extent necessary for the determination of an undistorted value of $(k_L a)$ by the dynamic method. It is thus obvious that a mathematical description of the dynamics of the probe must account for the effects of individual above listed resistances. However, more detailed analyses have revealed that additional peculiar effects may appear during start-up of a "first-order process" (e.g. during start-up of aeration and mixing in fermentors¹), or that an interaction of the probe with bubbles of the batch may eventually appear^{1,3,4}.

In this work we have put more emphasis on developing a faithful relationship between $(k_L a)$ and the response of the probe. This calls, of course, for a full command of the dynamics of the probe. Special attention has been focused on the analysis of the probes manufactured by Vývojové dílny of the Czechoslovak Academy of Sciences in view of their prospective wide use. Newly we have described and explained the slowdown in the last 20% of the response of the probe, often observed by other authors⁵⁻⁸.

MODELS OF PROBE DYNAMICS

Empirical model

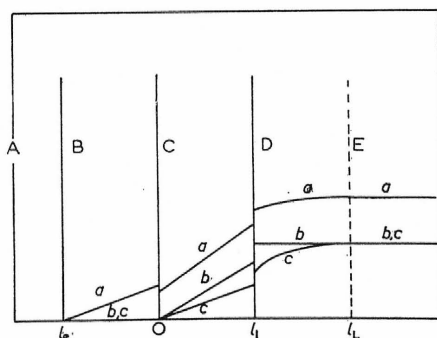
For a normalized response, Γ , of the probe to an arbitrary continuous concentration change, $G(t)$, Mueller and coworkers⁹ have derived the following relation using the principle of superposition of the solution in linear systems of partial differential equations

$$\Gamma(t) = G(0) \Gamma^1(t) + \int_0^t \Gamma^1(t - \lambda) \frac{dG(\lambda)}{d\lambda} d\lambda. \quad (1)$$

For the description of the dynamics of the probe proper, Mueller and coworkers⁹

FIG. 1
Typical Oxygen Concentration Profile in Individual Layers Covering the Cathode of an Oxygen Probe. Resistance to oxygen transfer is concentrated: a) in all layers, b) in the membrane of the probe, c) in the membrane and the adhering film.

A electrode, B electrolyte, C membrane, D liguid film, E bulk of liquid



have proposed a first-order model with time-delay leading to the following relation for the normalized response, Γ^1 , to a unit concentration step change

$$\Gamma^1 = 1 - \exp(-kt). \quad (2)$$

The same model (2) has been used also by Fuchs and Ryu¹⁰. Eq. (2) is only approximate as it offers unsatisfactory results for low values of Γ^1 (from 0 to 0.25) and for certain types of probes also for high values of Γ^1 (from 0.8 to 1), which is a fact to which the authors themselves drew attention (see Fig. 2 taken over from their work). The idea of using time-delay terms can be applied also to more complex systems where, apart from the delay of the probe alone, we have to account also for the delay of the recording device, which can be achieved also by a first-order time-delay term¹¹. This approach, however, does not contribute qualitatively anything new.

In ref.¹¹ it was shown that models of the dynamics of the probe using first-order time-delay terms do not provide correct values of the volumetrical mass transfer coefficient. The error is the greater the slower the probe and the higher the measured ($k_L a$) (Fig. 3 and 4 taken over from ref.¹¹). Unfortunately, these are just the conditions where the distortion due to the dynamics of the probe becomes most effective. This lead us to the conclusion that such models do not describe the dynamics of the probe proper correctly and were not therefore used for computer evaluation of the response curves.

Rational Models

This group of models derives from the assumptions on the mechanism of mass transfer between the bulk phase in which the concentration of oxygen is measured and the cathode of the electrode system of the probe. Mancy and coworkers¹² were first to use the one-dimensional model of oxygen diffusion in the membrane and the film

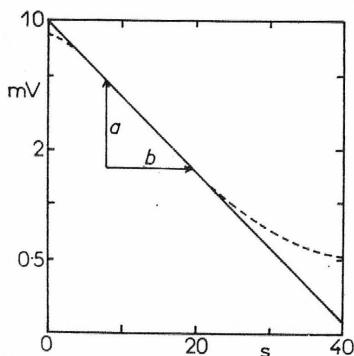


FIG. 2
Response Time Curve for a Step Change in Dissolved Oxygen Concentration from Saturation to Zero (taken from ref.⁹)
—— Assumed, - - - - - observed, $1/t_0 = 2.303a/b$.

of electrolyte in order to describe the dynamics of the probe. This model is often termed "the single-diffusion layer model". This model was used later with minor modification by Aiba and coworkers^{13,14}, Benedek and Heideger⁶ Heineken¹⁵ and Linek and coworkers¹. The resulting relation for the normalized response of the probe to a unit concentration step change takes the form

$$\Gamma^1 = 1 - 2 \exp(-kt) + 2 \sum_{n=2}^{\infty} (-1)^n \exp(-n^2 kt). \quad (3)$$

k is a constant of the probe which may be determined *e.g.* from the slope of the linear part of the plot of $\ln(1 - \Gamma^1)$ versus time (*i.e.*, at higher values of time when the sum of the infinite series in Eq. (3) is negligible).

For the case of a significant resistance to mass transfer being not only in the membrane and the electrolyte layer but also in the film of liquid adjacent to the membrane, the following expression was derived³

$$\Gamma^1 = 1 - 2(L + 1) q_1 \exp[-(\beta_1/\pi)^2 kt] - 2 \sum_{n=2}^{\infty} q_n(L + 1) \exp(-y_n kt), \quad (4)$$

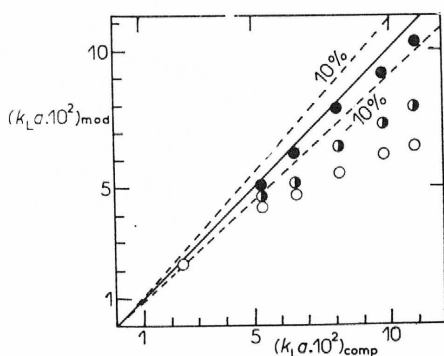


FIG. 3

A Comparison of the Volumetric Mass Transfer Coefficient Computed from Models and Determined by the Bubbling Method (taken from ref.¹¹)

○ Without considering the dynamics of the probe proper; ● model (1) due to Fuchs and Ryu¹⁰, ● model (3) from ref.^{1,6,13-15}. Used probe: Hospodka and Čáslavský¹⁶ with a 25 μm polypropylene membrane; probe constant $k = 0.1602 \text{ s}^{-1}$.

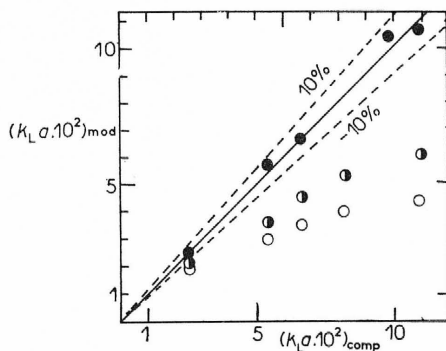


FIG. 4

A Comparison of the Volumetric Mass Transfer Coefficient Computed from Models and Determined by the Bubbling Method (taken from ref.¹¹).

Used probe: Hospodka and Čáslavský¹⁶ with 15 μm polypropylene membrane; probe constant $k = 0.9211 \text{ s}^{-1}$.

where $y_n = (\beta_n/\pi)^2$ and $q_n = \beta_n/[\sin \beta_n(L + L^2 + \beta_n^2)]$. β_n are positive roots of equation

$$\beta \cotg \beta = -L. \quad (5)$$

L is a parameter characterizing the resistance of the liquid film, defined as a ratio of the resistance to mass transfer in the membrane and the electrolyte layer to that of the liquid film adjacent to the membrane. Its value can be determined experimentally from the reading of the probe in air, M_A , in nitrogen, M_N , and in air-saturated liquid, M_L , under the given hydrodynamic conditions from the relation³

$$L = (M_L - M_N)/(M_A - M_L). \quad (6)$$

If the liquid film resistance is negligible ($L \rightarrow \infty$), Eq. (4) reduces to the earlier derived Eq. (3). The other asymptotic case ($L = 0$, the resistance of the membrane and the electrolyte layer being negligible) corresponds to oxygen probes without membrane. There have been attempts recently to use such electrodes for detecting the course of fermentation processes.

It has been found⁸ that a simple single-diffusion layer model, Eq. (3) or (4), describes the experimental course of the response in the whole region of Γ^1 only for some types of oxygen probes. For other types the agreement is poor for high values of Γ^1 . The response of these electrodes lags in comparison with the model during the last 10 to 20% of the response. Benedek and Heideger⁵ suggested that this may be the result of side diffusion of oxygen toward the cathode and of the nonuniform thickness of the membrane. Kok and Zajic⁷ proposed a central well model incorporating a lateral diffusion of oxygen from the anodic compartment to the cathode. They derived the following relation for the normalized response of the probe to a unit concentration step change

$$\Gamma^1 = (1 - C) \left\{ 1 - \frac{2E}{\sqrt{\pi t}} \sum_{n=0}^{\infty} \exp \left[-\frac{E^2}{4t} (2n + 1)^2 \right] \right\} + C \left[\frac{\operatorname{erfc} [F/\sqrt{(t + A)}] - \operatorname{erfc} (F/\sqrt{A})}{\operatorname{erfc} (F/\sqrt{A})} \right]. \quad (7)$$

E , F and C are model parameters. A is the time of exposure of the probe to the original oxygen concentration prior to the step change. The central well model appears rather complicated from the mathematical point of view although it is capable of describing even the slowdown in the final stage of the response. For its complexity the corresponding relation for the response during dynamic measurements has not been derived and thus the model appears rather inconvenient for computer evaluation of $(k_1 a)$ from the response curves.

Using the concept of the mechanism of mass transfer through nonuniformly thick membranes and layers of electrolyte we have derived⁸ a multi-diffusion layer, multi-region model of the dynamics of the probe leading to the following expression for the normalized response of the probe to a unit concentration step

$$\Gamma^1 = 1 + 2 \sum_{r=1}^s A_r \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 k_r t), \quad \sum_{r=1}^s A_r = 1. \quad (8)$$

The model contains $(s - 1)$ parameters A_r and s parameters k_r . The majority of probes exhibiting the slowdown can be described with the single-diffusion layer, two-region model, which mean that $s = 2$. Similarly as the model of Kok and Zajíc⁷, Eq. (7), this model, Eq. (8), describes the real response very well in the whole region of Γ^1 values. The model, Eq. (8), is simpler and more convenient for computer processing, than Eq. (7). Eq. (8) is actually a linear combination of s relations for the simple single-diffusion layer model, Eq. (3), to which Eq. (8) reduces for $s = 1$.

COMPARISON OF MODELS WITH REAL RESPONSE

From comparison of the real responses of the probes with those computed from models, one can determine which set of models is adequate and sufficient for description of the behaviour of any probe under all interesting conditions. Fig. 5 shows schematically some types of currently available probes. The figure does not show the probe manufactured by Monokrystaly (Turnov), Czechoslovakia, as it is very

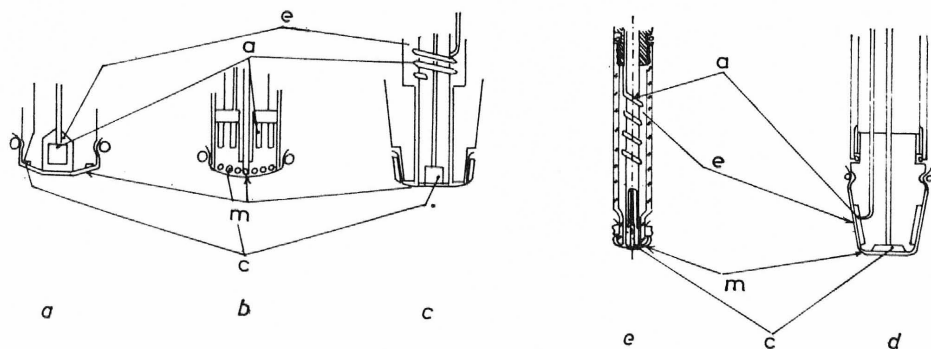


FIG. 5

Types of Oxygen Probes

a) Yellow Springs Instrument Co., Model G-1678.5, b) galvanic type of Borkowski and Johnson²⁴, c) Čerkasov²⁵ probe, d) Hospodka and Čáslavský probe¹⁶, e) Vývojové dílny, Czechoslovak Academy of Sciences (1976).

similar in construction to the probe designed by Hospodka and Čáslavský¹⁶ and its dynamic behaviour is the same³ as that of the Čerkasov modification of Clark's probe with a 3 mm in diameter cathode. The probe manufactured by Vývojové dílny of Czechoslovak Academy of Sciences is a copy of Čerkasov's probe with a 1 mm cathode. The responses of some types of the probes shown in Fig. 5 to a unit concentration step change are shown in Fig. 6a, 6b and 7, and compared with those computed from models. For the description of the dynamics of the probes due to Čerkasov, Hospodka and Čáslavský and the Turnov probe one can do with the simple single-diffusion layer model (3) while for other probes one has to resort to multi-region models, Eq. (8). From the latter probes, the dynamics of the probe of Borkowsky, of the YSI probe with uniformly stretched membrane and the probe manufactured by Vývojové dílny of Czechoslovak Academy of Sciences can be sufficiently accurately described by the two-region model with three parameters (A_1 , k_1 and k_2). The behaviour of the YSI probe with nonuniformly stretched membrane calls for multiple-region model with more than three parameters ($s > 2$).

The step concentration changes required by the above mentioned experiments were realized by switching the feed gas (oxygen for nitrogen by turning a three-way cock) surrounding the membrane under the conditions of negligible resistance in the liquid film adjacent to the membrane. As a disadvantage of this approach appears that the temperature of the streaming gases is difficult to control and often one cannot be sure that the measurements take place at the required temperature. Unfortunately, the temperature dependence of the dynamics of the probe is strong¹.

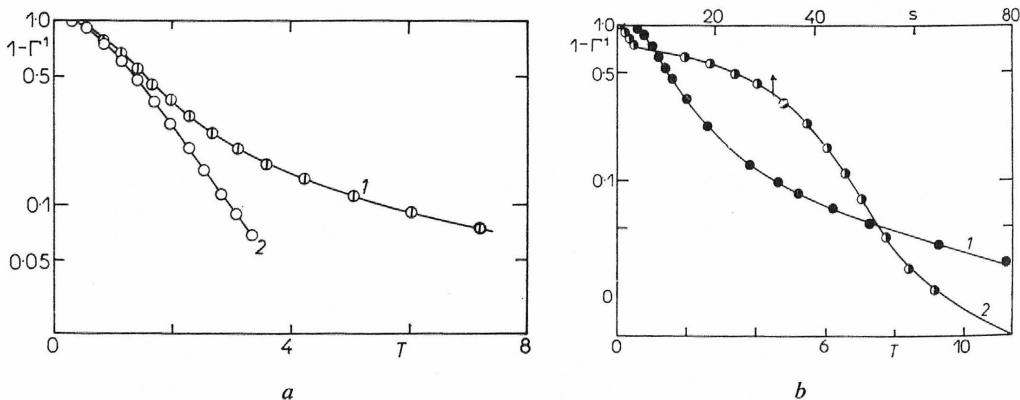


FIG. 6

A Comparison of Computed and Experimental Responses to a Unit Step Change

a 1 Čerkasov probe²⁵ — single-diffusion layer model, $k = 1.38 \text{ s}^{-1}$, 2 Borkowski and Johnson probe²⁴ — two-region, single-diffusion layer model, $k_1 = 0.033 \text{ s}^{-1}$, $k_2 = 0.00558 \text{ s}^{-1}$, $A_1 = 0.871$. *b* 1 YSI probe — uniformly stretched membrane, two-region, single diffusion layer model $k_1 = 0.504 \text{ s}^{-1}$, $k_2 = 0.833 \text{ s}^{-1}$; 2 YSI Probe — nonuniformly stretched membrane.

This is the reason for which the concentration change is more often realized by transferring the probe from one vessel filled with air- or oxygen-saturated water into another containing nitrogen-saturated water (eventually with addition of sodium sulphite keeping zero oxygen concentration). During measurements in liquids, however, a resistance to oxygen transfer may appear within the liquid film adjacent to the membrane. The decision whether the resistance in this film under given experimental conditions is or is not significant can be made on the basis of an experiment consisting in turning on the electrode in a vessel filled with oxygen-saturated water. If the response of the probe is independent of the position of the probe in the vessel, it may be inferred that the film resistance is negligible. We found out that for fast probes ($k > 0.8 \text{ s}^{-1}$) the resistance of the liquid film was significant even in a 100 ml beaker stirred at 100 rpm by a magnetic stirrer and with a gas being bubbled through the liquid. Fig. 8 shows the responses of the Čerkasov probe (3 mm in diameter cathode) measured under various velocities of liquid past the membrane. The time dependence of the $\ln(1 - \Gamma^1)$ values is similar to that measured at a negligible resistance in the liquid film. At sufficiently high values of time the dependence is linear, similarly as in the case of Eq. (3). Should, however, the experimenter

FIG. 7

A Comparison of Experimental and Computed Responses to a Unit Step Change from the Single-Diffusion Layer, Two-Region Model (8) for Probe Manufactured by Vývojové dílny, Czechoslovak Academy of Sciences, $k_1 = 0.260 \text{ s}^{-1}$, $k_2 = 0.0674 \text{ s}^{-1}$, $A_1 = 0.926$

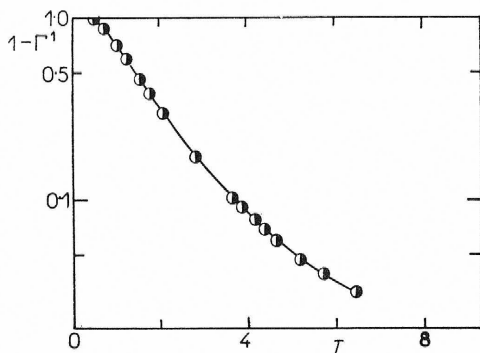
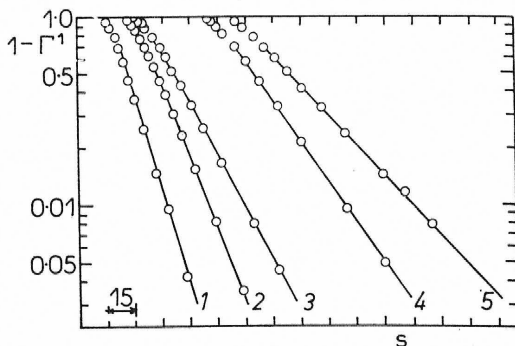


FIG. 8

$(1 - \Gamma^1)$ versus Time Plot for Various Values of Parameter L (taken from ref.¹⁷)

1 $L \rightarrow \infty$, 2 $L = 7.41$, 3 $L = 2.3$, 4 $L = 1.12$, 5 $L = 1.07$.



identify the value of the slope found under these conditions from the linear part of the dependence, k^+ , with the constant of the probe, k (as was the case of model given by Eq. (3)), he would be in error. This is so because Eq. (4) indicates the following relationship between k and k^+

$$k^+ = (\beta_1/\pi)^2 k . \quad (9)$$

Eq. (9) has been tested experimentally^{3,17}. A comparison of k found experimentally under the conditions of negligible resistance in the liquid film with that computed from Eq. (9) and the experimentally determined slope k^+ for various parameters L (β_1 is the first positive root of Eq. (5)) is furnished in Fig. 9 for experiments performed in 90% water solution of glycerol¹. It is apparent that Eq. (4) well describes the effect of the resistance of the liquid film on the dynamics of the probe over sufficiently wide range of L . For illustration: If the signal of the probe drops due to the resistance of the liquid film by 20% of the value corresponding to the signal under the conditions of negligible film resistance there follows from Eq. (6) that $L = (0.8 - 0)/(1 - 0.8) = 4$. From Fig. 9 it is apparent that the model is capable of describing the effect of the hydrodynamics of the probe up to a 50% decrease of the signal of the probe.

We thus conclude that set of models given by Eqs (3), (4) and (8) for $s = 2$ closely describe the dynamic response of all available oxygen probes to experimental realization of a unit concentration step both in the gas and in liquid with eventual presence of the resistance in the liquid film adhering to the membrane.

THE RESPONSE OF THE PROBE DURING DYNAMIC METHOD MEASUREMENTS

Transient course of liquid phase concentration of dissolved oxygen during measurement of the volume mass transfer coefficient ($k_L a$) by a dynamic method can be obtained by integrating the appropriate rate equation for absorption of oxygen in

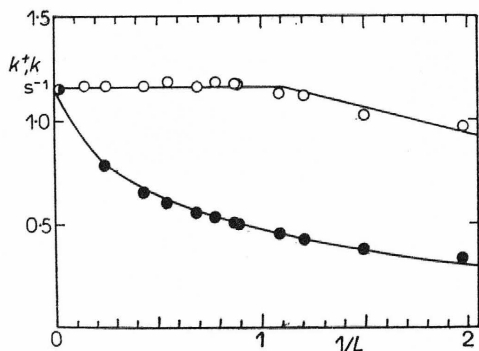


FIG. 9
Slope k^+ and Constant of Probe k Computed from Eq. (9) as Functions of Parameter L
● Gas phase value of k , i.e. for $L \rightarrow \infty$,
● value of k^+ , ○ value of k computed from Eq. (9).

the system. For a liquid phase batch bubble reactor and the absorption being accompanied by a very slow reaction taking place solely in the bulk phase this equation takes the form

$$dc/dt = k_L a(c^+ - c) - r, \quad (10)$$

where r is the rate of oxygen conversion by the reaction (*e.g.* by respiration of micro-organisms or by chemical reaction). Usually it is assumed that both gas and liquid are ideally mixed (then c^+ is the equilibrium concentration of oxygen with respect to the outlet gas composition) and that $(k_L a)$, the equilibrium concentration c^+ and temperature remain constant throughout the measurement of the response. This need not be always satisfied. Under the given conditions the integration of Eq. (10) with the initial condition $c = c_0$ at $t = 0$ leads to the following exponential expression for oxygen concentration

$$c = I(1 - \exp(-Kt)) + c_0, \quad (11)$$

$$I = c^+ - r/(k_L a) - c_0, \quad (12)$$

$$K = k_L a \quad (13)$$

provided the absorption is not accompanied by a chemical reaction ($r = 0$), or, is accompanied by a zero-order reaction only^{1,18} (*e.g.* respiration, $r = \text{const.}$) For a first-order reaction¹⁹ ($r = k^1 c$) we obtain

$$I = c^+(k_L a)/(k^1 + (k_L a)) - c_0, \quad (14)$$

$$K = k_L a(1 + k^1/(k_L a)).$$

In experiments with a first-order reaction with respect to oxygen in closed reactors ($k_L a = 0$) the balance (10) takes the form: $dc/dt = -k^1 c$. Its integration with the initial condition $c = c_0$ at $t = 0$ leads again to Eq. (11) where $K = k^1$ and $I = -c_0$. An example of this type of measurement may be the determination of the reaction rate constant for enzyme oxidation of glucose in solution by dissolved oxygen in the presence of glucose oxidase enzyme²⁷. At a zero time a dosis of enzyme is injected into the closed reactor filled with oxygen-saturated solution of glucose and the course of oxygen concentration in the batch is detected by the oxygen probe.

The same exponential function, Eq. (11), has been derived² also for the transient development of oxygen concentration in liquid draining from an absorption column during measurement of $(k_L a)$ by the dynamic method. Assuming plug flow of both phases and both streams to be initially mutually at equilibrium with respect to oxygen concentration, the oxygen concentration in the draining liquid following a sudden

change of inlet gas concentration obeys the relation (11). In this equation $I = c_1^+$ is the concentration of oxygen in liquid in equilibrium with the entering gas, $c_0 = 0$ and further

$$K = (k_L a) u_g u_l / V_L (u_g + u_l), \quad (15)$$

u_g and u_l are superficial velocities of gas and liquid in the column.

Under the above simplifying assumptions the dynamic methods of measurement always lead to the following of the exponential type of concentration change, given by Eq. (11). In the following paragraph we shall present responses of the oxygen probes to the exponential concentration change given in Eq (11) only for those models of the probes that have been found suitable for computer evaluation.

MODELS WITH THE IDEAL EXPONENTIAL CONCENTRATION CHANGE

For a simple single-diffusion layer model, Eq. (3), numerous authors^{1,5,13-15} have derived the following formula for the normalized response of the probe, Γ , to the exponential concentration change, Eq. (11)

$$\Gamma = 1 - \frac{\pi\sqrt{B}}{\sin(\pi\sqrt{B})} \exp(-Bkt) - 2 \sum_{n=1}^{\infty} (-1)^n \frac{\exp(-n^2 kt)}{n^2/B - 1} \quad (16)$$

where

$$B = K/k. \quad (17)$$

For the case when a significant resistance resides in the liquid film adjacent to the membrane the following relation has been derived³

$$\Gamma = 1 + 2(L+1) \sum_{n=1}^{\infty} q_n \left[\frac{\exp(-Bkt)}{B/y_n - 1} + \frac{\exp(-y_n kt)}{y_n/B - 1} \right]. \quad (18)$$

In view of the fact that viscosity of fermentation broths is usually high there is a strong probability of a significant resistance on the side of the liquid film. It turns out that the resistance in the film of liquid adhering to the membrane of the probe in a fermentation broth may be neglected only for small probes equipped with thick membranes^{20,21}.

For the multi-diffusion layer model of the probe, Eq. (8), the following relation has been derived for the normalized response to the exponential concentration change given by Eq. (11):

$$\Gamma = 1 - \sum_{r=1}^s A_r \left[\frac{\sqrt{B_r} \pi}{\sin(\pi\sqrt{B_r})} \exp(-B_r k_r t) + 2 \sum_{n=1}^{\infty} (-1)^n \frac{\exp(-n^2 k_r t)}{n^2/B_r - 1} \right] \quad (19)$$

Similarly as in the case of the response to the step concentration change, this relation is also a mere linear combination of s relations for the response of the single-diffusion layer model, Eq. (16).

MODELS WITH NONIDEAL EXPONENTIAL CONCENTRATION CHANGE

Measurements in dispersions. Commonly it is assumed that the signal of the probe immersed into a dispersion of gas in liquid corresponds to the concentration of oxygen dissolved in the liquid phase. However, it has been established^{17,20,21} that the signal of the probe may be somewhat distorted unless both phases are at equilibrium. If the partial pressure of oxygen in gas is higher than the equilibrium oxygen pressure in liquid, the signal of the probe may be higher than that corresponding to the dissolved oxygen. Votruba and Sobotka⁴ introduced the assumption that the signal of the probe in a dispersion, M_D , is the weighted average of probe's reading in liquid, M_L , and in gas, M_G , with the local volume fraction of the appropriate phase used as the weight

$$M_D = M_G x_g + M_L (1 - x_g). \quad (20)$$

According to our opinion this model is too much simplified: It does not account for the dynamics of the probe proper although it is more expressive here than for the measurement of $(k_L a)$ (interactions take place within several hundreds of a second). Further, it does not respect the existence of the liquid film separating the bubble from the membrane (the studies of coalescence indicate that such film always exists, at least for a few tens of seconds) and, especially the distribution of the surface area and the time of exposure of the cathode to bubbles. For this reason we have decided to carry out our own experimental verification of validity of the model.

The measurements were carried out in an aerated vessel 140 mm in diameter equipped with four radial baffles, mixed by a six-blade turbine 50 mm in diameter at 1000 rpm. The vessel was filled with 4 litres of 1M solution of sodium sulphite ($\text{pH} \approx 9$) with an addition of 10^{-4} kmol of CoSO_4 per cubic meter as catalyst. The accompanying chemical reaction under these conditions is sufficiently fast to maintain the concentration of oxygen in liquid phase at a zero value²². Pure oxygen was fed into the space below the turbine at the rate of 4 litres per minute. The mean volume content of gas phase in the dispersion amounted to $x_g = 0.12$ (computed from the elevation of the level of the batch). The oxygen probe used (Vývojové dílny, Czechoslovak Academy of Sciences) in the experiments was located 3 cm over the bottom, in the level of the impeller, and 4 cm below the liquid level; in all three cases the surface of the cathode was faced to the bottom. Near the bottom and in the level of the impeller the signal of the probe was equal to zero and free of the fluctuations, but in the position near the liquid level the signal fluctuated in the interval 0–0.52

(the reading normalized with respect to the reading of the probe in pure oxygen). According to Eq. (20) recommended by Votruba and Sobotka⁴ the reading of the probe should have range around 0.12. In another our paper¹⁷ (further see also ref.²⁰⁻²⁵) it was shown that the reading of the probe depends considerably on its position in the fermentor. Moreover, the founded dependence did not correspond to the distribution of the volume fraction of the dispersed gas, x_g .

Thus not only that the model of interaction, as presented by Votruba and Sobotka⁴, does not agree with the empirical facts, but it cannot be even improved significantly by taking into account the so far neglected facts. In this respect it is recommended that, instead of complex modelling the undesirable interaction, this be experimentally suppressed in the simplest possible manner. The interaction can be eliminated for instance by suitable design of the probe and its proper location in the vessel. For this purpose one can use centrifugal and inertia forces and locate the probe in the by-pass or into the bulk stream of liquid in the vessel so as to shield the cathode from undesirable contact with bubbles by the body of the probe.

These empirical methods have already been successfully used¹⁷.

THE START-UP PERIOD OF AERATION AND MIXING IN A FERMENTOR

In the derivation of the relations for the dynamic methods of measurement of $(k_L a)$ it is usually assumed that after the starting of the aeration and mixing $(k_L a)$ reached instantaneously the equilibrium value. This, however, need not be always the case. It is apparent that there is a definite time required for the interfacial area of bubbles in the dispersion to reach its steady-state value. This time is the longer the greater the gas hold-up in the batch. The importance of this problem is illustrated by the following example presented in ref.¹⁷: The steady-state gas hold-up in a fermentor amounted to $V = 1.3 \cdot 10^{-3} \text{ m}^3$ at the gas feed rate $\dot{V}_G = 1.48 \cdot 10^{-4} \text{ m}^3 \text{ s}^{-1}$. From this it is obvious that the steady-state interfacial area cannot be reached prior to the time $\tau = V/\dot{V}_G = 8.78 \text{ s}$. The time τ is termed the start-up period. In the paper¹⁷ it was shown that under the given experimental conditions the steady-state value of $(k_L a)$ amounted to 0.11 s^{-1} and hence during the start-up period the liquid phase was saturated to 60%. This indicates that more than one half of the response was distorted.

Although the effect of the start-up period due to the time dependence of gas hold-up after the starting of aeration and mixing may be eliminated by proper experimental method (*e.g.* the fed is suddenly switched for a gas of different oxygen concentration, (most often oxygen for nitrogen, without interrupting the mixing) but this method brings other problems associated with the lack of knowledge of segregation and gas-phase mixing as shown in ref.²⁰.

Assuming linear dependence of the volumetric mass transfer coefficient on time during the start-up period, *i.e.* assuming that K in Eq. (11) is $K = (k_L a) t/\tau$, the

following expression for the normalized response to the exponential concentration change, Eq. (11), has been derived¹⁷

$$\Gamma = \Gamma_{(18)} - \Gamma_{\text{cor}}.$$

$\Gamma_{(18)}$ is the normalized response to the ideal exponential concentration change given in Eq. (18) and

$$\Gamma_{\text{cor}} = 2(L + 1) \sum_{n=1}^{\infty} q_n \left[\frac{\exp(-Bkt)}{B/y_n - 1} + \frac{\exp(-y_n kt)}{y_n/B - 1} + \exp(-y_n kt) \left(1 + y_n \int_0^{kt} \exp\left(y_n u - \frac{B}{W} u^2\right) du \right) \right] \quad (22)$$

for $0 \leq t \leq \tau$ and

$$\Gamma_{\text{cor}} = 2(L + 1) \sum_{n=1}^{\infty} q_n \exp(-y_n kt) \left[\frac{\exp(W(y_n - B)) - 1}{B/y_n - 1} + y_n \int_0^{kr} \exp\left(y_n u - \frac{B}{W} u^2\right) du \right] \quad (23)$$

for $t \geq \tau$. W is a dimensionless duration of the start-up period, $W = k\tau$.

COMPUTER EVALUATION OF THE RESPONSE OF THE OXYGEN PROBE TO THE UNIT AND EXPONENTIAL CHANGE

Using the principle of superposition of the solution of a linear partial differential equation (Eq. (2)) theoretical expressions have been derived in the preceding text for the normalized response of the oxygen probe, $f = (1 - \Gamma)$, as a function of time and parameters characterizing the properties of the probe, hydrodynamic resistance of the liquid film and the effect of the start-up period.

From the standpoint of measurement of K we have two types of responses of the probe:

a) response to a unit step concentration change of the form

(a1) $f^1 = f^1(k, t, L, \tau)$ for the single-diffusion layer model of the probe

or, as a particular case

(a2) $f^1 = f^1(k_1, k_2, A, t)$ for the single-diffusion layer two-region model of the probe ($L \rightarrow \infty, \tau = 0$).

Based on the optimal approximation (from the view point of minimum sum of square deviations) of the measured data by the appropriate expression of the type (a1) or (a2), values of k, k_1, k_2, A , characterizing the dynamic properties of the probe (L and τ are known input parameters), are determined.

b) response to an exponential concentration change of the form

$$(b1) f = f(K, t, k, L, \tau)$$

or

$$(b2) f = f(K, t, k_1, k_2, A) \quad \text{for } L \rightarrow \infty, \tau = 0.$$

Optimum approximation of the experimental data by the appropriate expression of the type (b1) or (b2) leads to a value of K . (L and τ are known input parameters; k or k_1, k_2 and A have been found from expressions (a1) or (a2)).

This technique of data processing was preferred to other methods. Such methods are based on the use of a chosen characteristic of the response curve (*e.g.* the value of some of the first moments of the response curve³ or a position of *e.g.* inflection^{26,27} point) and thus make use of only a small portion of the information carried in the response curve. For instance, two different response curves may have some of their moments equal, yet this difference neglected by moment methods is well discernible by the above outlined method.

The principal advantage of the here used technique, in contrast to other alternative methods^{3,26}, is its maximum sensitivity. This is accomplished by independent determination of the dynamics of the probe through an independent experiment (evaluated from the response to a unit concentration step change). The resulting value of ($k_L a$) is thus burdened by the least experimental error. This, of course, at the expense of more laborious data processing.

Definite forms of the expressions applicable to the individual treated cases are summarized in Table I. In view of the arbitrariness of adjustment of the zero time instant and the uncertainty of experimental determination of this instant, the time is considered in the theoretical equations as the floating coordinate. Instead of the current time t , the time coordinate is referred to an initially unknown instant t_0 , *i.e.* as $(t - t_0)$. In all expressions presented in Table I we thus have one extra parameter, t_0 , to be sought by the optimization technique. Table II presents a review of the known input and sought output parameters of individual models.

RESULTS OF COMPUTER EVALUATION OF THE RESPONSES

The results of the evaluations of the responses of the oxygen probes to a sudden and exponential oxygen concentration change during measurements of ($k_L a$) in a bubble reactor have been presented in Table III for various experimental conditions and models used. The table also gives for each type of the model the reference where the

TABLE I

Review of Model Responses

Single-diffusion layer, two-region model with negligible resistance in liquid film ($L \rightarrow \infty$)	$\left\langle \begin{array}{l} \text{response to step change} \\ \text{exponential change} \end{array} \right.$		$f = f_1$
			$f = f_2$
Single-diffusion layer model with resistance in liquid film	$\left\langle \begin{array}{l} \text{step change} \\ \text{exponential change} \end{array} \right.$		$f = f_3$
			$f = f_4$
Single-diffusion layer model with resistance in liquid film, accounting for the effect of the start-up period	$\left\langle \begin{array}{l} \text{step change} \\ \text{exponential change} \end{array} \right.$	$t < \tau$	$f = f_{5a}$
		$t \geq \tau$	$f = f_{5b}$
	$\left\langle \begin{array}{l} \text{step change} \\ \text{exponential change} \end{array} \right.$	$t \leq \tau$	$f = f_{6a}$
		$t \geq \tau$	$f = f_{6b}$

$$f_1 = -2[A \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 k_1(t - t_0)) + (1 - A) \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 k_2(t - t_0))]$$

$$f_2 = A \left[\frac{\sqrt{K/k_1} \cdot \pi}{\sin(\pi \sqrt{K/k_1})} \exp(-K(t - t_0)) + 2 \sum_{n=1}^{\infty} (-1)^n \frac{K \exp(-n^2 k_1(t - t_0))}{n^2 k_1 - K} \right] +$$

$$+ (1 - A) \left[\frac{(\sqrt{K/k_2}) \cdot \pi}{\sin(\pi \sqrt{K/k_2})} \exp(-K(t - t_0)) + 2 \sum_{n=1}^{\infty} (-1)^n \frac{K \exp(-n^2 k_2(t - t_0))}{n^2 k_2 - K} \right]$$

$$f_3 = C \sum_{n=1}^{\infty} Q_n \exp(-Y_n k(t - t_0)); \quad L = \begin{cases} (0, \infty) \\ \infty \\ 0 \end{cases}$$

$$f_4 = -C \left[\exp(-K(t - t_0)) \sum_{n=1}^{\infty} \frac{k Q_n Y_n}{K - k Y_n} + \sum_{n=1}^{\infty} \frac{K Q_n}{k Y_n - K} \exp(-Y_n k(t - t_0)) \right];$$

$$L = \begin{cases} (0, \infty) \\ \infty \\ 0 \end{cases}$$

$$f_5 = \begin{cases} 1 - \frac{t - t_0}{\tau} + \frac{C}{k\tau} \sum_{n=1}^{\infty} \frac{Q_n}{Y_n} (1 - \exp(-Y_n k(t - t_0))); & (t - t_0) \leq \tau \\ \frac{C}{k\tau} \sum_{n=1}^{\infty} \frac{Q_n}{Y_n} [\exp(-Y_n k(t - t_0)) - \exp(-Y_n k(t - t_0))]; & (t - t_0) \geq \tau \end{cases} \quad L = \begin{cases} (0, \infty) \\ \infty \\ 0 \end{cases}$$

TABLE I
(Continued)

$$f_6 = \begin{cases} C \sum_{n=1}^{\infty} Q_n \exp(-Y_n k(t-t_0)) \left(1 + Y_n \int_0^{k(t-t_0)} \exp\left(Y_n u - \frac{K}{k^2 \tau} u^2\right) du\right); & (t-t_0) < \tau \\ -C \exp(-K(t-t_0)) \sum_{n=1}^{\infty} \frac{k Q_n Y_n}{K - k Y_n} + \sum_{n=1}^{\infty} Q_n \exp(-Y_n k(t-t_0)) \cdot \\ \cdot \left\{ \frac{K}{k Y_n - K} - \frac{k Y_n (1 - \exp(\tau Y_n - K/k))}{k Y_n - K} - \right. \\ \left. - Y_n \int_0^{k\tau} \exp\left(Y_n u - \frac{K}{k^2 \tau} u^2\right) du \right\}; & (t-t_0) \geq \tau \end{cases}$$

$$L = \begin{cases} (0, \infty) \\ \infty \\ 0 \end{cases}$$

For $L \rightarrow \infty$

$$-C \sum_{n=1}^{\infty} \frac{k Q_n Y_n}{K - k Y_n} = \frac{\pi \sqrt{K/k}}{\sin(\pi \sqrt{K/k})}$$

Here for $0 < L < \infty$: $C = 2 + 2L$; $Q_n = a_n$; $Y_n = y_n$

$L \rightarrow \infty$: $C = -2$; $Q_n = (-1)^n$; $Y_n = n^2$

$L = 0$: $C = -2/\pi$, $Q_n = (-1)^n/(n - 0.5)$, $Y_n = (n - 0.5)^2$

$a_n = \beta_n / (L + L^2 + \beta_n^2) \sin \beta_n$, β_n are positive roots of $\beta \cotg \beta + L = 0$.

TABLE II
Summary of Parameters in Individual Models

Type	Dependent variable	Independent variable	Known input parameters	Unknown and sought parameters
1	t	$(1 - \Gamma^1) : f_1$	—	A, k_1, k_2, t_0
2	t	$(1 - \Gamma) : f_2$	A, k_1, k_2	K, t_0
3	t	$(1 - \Gamma^1) : f_3$	L	k, t_0
4	t	$(1 - \Gamma) : f_4$	k, L	K, t_0
5	t	$(1 - \Gamma^1) : f_5$	L	k, t_0
6	t	$(1 - \Gamma) : f_6$	k, L, τ	K, t_0

reader can find detailed description of the apparatus and experimental technique of measurement of the response. The models well approximate the true course of the curves in the whole range. The relative deviations of experimental points from the computed dependence did not exceed for any of the examined responses 2.8% (for the mean value of the relative variance see Table III). For illustration some of the experimental and model responses are shown in Fig. 10.

The results of response evaluations using incorrect models are summarized in Table IV. and Fig. 11. From these it is apparent that the determination of $(k_1 a)$ may be completely ruined if the multi-region character of the probe dynamics is overlooked and the one-region model f_3 is used instead of f_1 . If, however, the probe displays only a minor multi-region character (Čerkasov probe) the results of $(k_1 a)$ are not markedly influenced regardless of whether we use the expression f_1 or f_3 . Considerable error (k up to by 60% lower) may be committed in the determination of the

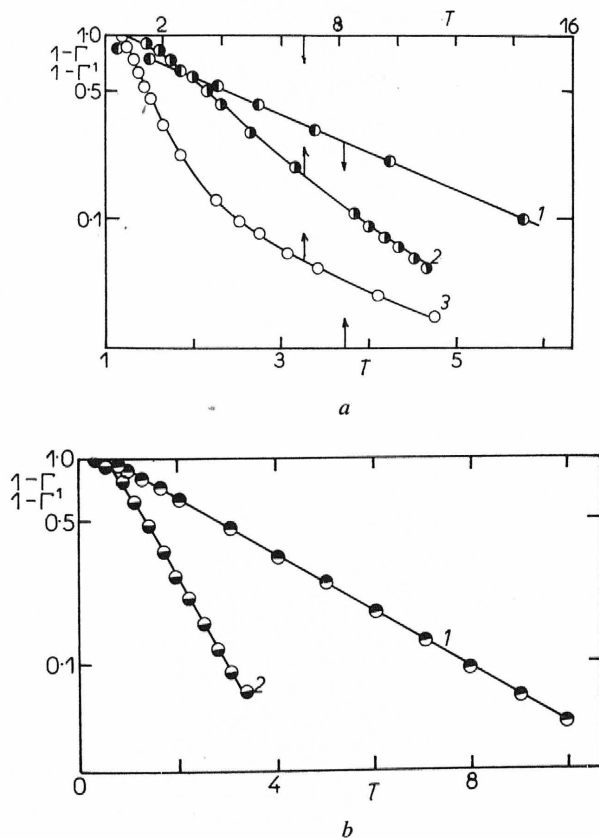


FIG. 10

A Comparison of Experimental and Model Responses (for meaning of symbols see Table III)
 a 3 No 4, 2 No 5, 1 No 6; b 2 No 7, 1 No 8.

constant of the probe k (for the one-region, single-diffusion layer model f_3) if the model with negligible resistance in the film adhering to the membrane ($L \rightarrow \infty$) is used for evaluation instead of the model respecting this resistance. Yet, maximum deviations of experimental points from the computed curves remain in both cases small ($\cdot 69\%$ and $\cdot 94\%$, see Tables III and IV). Also the error brought about by using model f_4 without the start-up period instead of f_6 leads to erroneous estimates of the volumetric mass transfer coefficient, especially at high value of $(k_1 a)$.

TABLE III

Results of Oxygen Probe Response Evaluation

 k_1, k_2, k and K are given in s^{-1} , τ in seconds.

No	Probe	Model	Input parameters	Sought parameters	S_y	Reference
1	Czechoslovak Academy of Sciences	f_1	—	$k_1 = 0.260$ $k_2 = 0.0673$ $A_1 = 0.926$	0.00591	(1)
2	Borkowski	f_1	—	$k_1 = 0.0337$ $k_2 = 0.0058$ $A_1 = 0.871$	0.00631	(1)
3	Borkowski	f_2	$k_1 = 0.0337$ $k_2 = 0.0058$ $A_1 = 0.871$	$K = 0.0177$	0.00928	(8)
4	YSI	f_1	—	$k_1 = 0.504$ $k_2 = 0.0833$ $A_1 = 0.909$	0.0286	(1)
5	YSI	f_2	$k_1 = 0.504$ $k_2 = 0.0833$ $A_1 = 0.909$	$K = 0.234$	0.0256	(8)
6	Čerkasov	f_3	$L = 1.447$	$k = 1.17^*$	0.00593	(17)
7	Čerkasov	f_3	$L \rightarrow \infty$	$k = 1.38$	0.0187	(1)
8	Čerkasov	f_4	$L \rightarrow \infty, k = 1.38$	$K = 0.157$	0.00383	(1)
9	Hospodka	f_6	$L \rightarrow \infty, k = 0.495, \tau = 8.77$	$K = 0.104$	0.0188	(1)
10	Hospodka	f_6	$L \rightarrow \infty, k = 0.495, \tau = 7.42$	$K = 0.0993$	0.0306	(1)
11	Hospodka	f_6	$L \rightarrow \infty, k = 0.549, \tau = 3.02$	$K = 0.0265$	0.00843	(1)
12	Hospodka	f_6	$L \rightarrow \infty, k = 0.495, \tau = 4.44$	$K = 0.0570$	0.0276	(1)

* The constant of the probe was measured also as a test under condition of negligible resistance in liquid film (i.e. in gas phase when $L \rightarrow \infty$) with the result: $k = 1.15 s^{-1}$.

Special attention thus has to be paid to the choice of the formula for evaluation. If one is in doubt as to whether a given probe displays multi-region behaviour, alternative calculations should be carried out in order to make the decision from comparison of the variances of experimental points about the computed curves (Tables III and IV).

TABLE IV
Results of Response Evaluations Summarized in Table III Using Incorrect Models

No ^a	Probe	Input parameters	Sought parameters	S _y	Model
7	Čerkasov	—	$k_1 = 1.58 \text{ s}^{-1}$ $k_2 = 1.2$ $A_1 = 0.635$	0.018	f_1
8	Čerkasov	$k^1 = 1.58 \text{ s}^{-1}$ $k_2 = 1.2 \text{ s}^{-1}$ $A^1 = 0.635$	$K = 0.157 \text{ s}^{-1}$	0.00372	f_2
4	YSI	$L \rightarrow \infty$	$k = 0.406 \text{ s}^{-1}$	0.0514	f_3
5	YSI	$L \rightarrow \infty, k = 0.406 \text{ s}^{-1}$	$K = 0.164 \text{ s}^{-1}$	0.0492	f_4
2	Borkowski	$L \rightarrow \infty$	$k = 0.0235 \text{ s}^{-1}$	0.0436	f_3
3	Borkowski	$L \rightarrow \infty, k = 0.235 \text{ s}^{-1}$	$K = 0.0141 \text{ s}^{-1}$	0.0296	f_4
9	Hospodka	$L \rightarrow \infty, k = 0.495 \text{ s}^{-1}$	$K = 0.124 \text{ s}^{-1}$	0.0179	f_4
10	Hospodka	$L \rightarrow \infty, k = 0.495 \text{ s}^{-1}$	$K = 0.113 \text{ s}^{-1}$	0.0169	f_4
11	Hospodka	$L \rightarrow \infty, k = 0.495 \text{ s}^{-1}$	$K = 0.0265 \text{ s}^{-1}$	0.00573	f_4
12	Hospodka	$L \rightarrow \infty, k = 0.495 \text{ s}^{-1}$	$K = 0.0591 \text{ s}^{-1}$	0.00846	f_4
6	Čerkasov	$L \rightarrow \infty$	$k = 0.563 \text{ s}^{-1}$	0.00863	f_3

^a The number corresponds to the reference number in Table III.

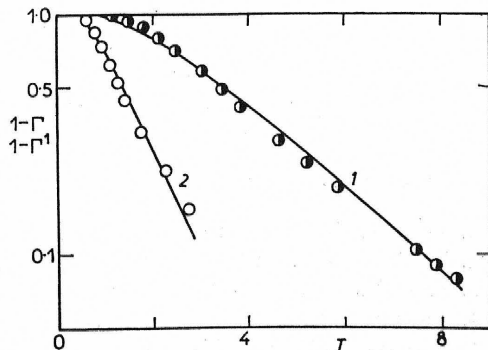


FIG. 11

A Comparison of Experimental Responses with those of Incorrect Models for YSI Probe

Unit step change (2, model f_3) and exponential concentration change (1, model f_4).

LIST OF SYMBOLS

a	surface area of dispersion per unit volume of liquid phase, specific interfacial area
A	time of contact of probe with gas
A_r	model parameter
B	$= K/k$
B_r	$= K/k_r$
c	liquid-phase oxygen concentration
c^+	equilibrium oxygen concentration
C	model parameter in Eq. (7)
E, F	model parameters in Eq. (7)
f_i, f_i^+	measured and computed value of normalized response
G	continuous change of oxygen concentration
I	defined by Eq. (12)
k	constant of probe
k^+	slope of linear part of $\ln(1 - \Gamma^1)$ versus time plot
k^1	reaction rate constant for a first-order reaction ($r = k^1 c$)
k_L	mass transfer coefficient
K	defined by Eqs (13), (14) or $= (k_L a) t/\tau$
L	model parameter characterizing the liquid film transfer resistance, see Eq. (6)
m	number of experimental points
M	reading of the probe; subscripts: A — air, D — dispersion, G — gas phase, L — liquid phase, N — nitrogen
q_n	$\beta_n / [\sin \beta_n (L + L^2 + \beta_n^2)]$
p	number of model parameters
r	reaction rate term in Eq. (10)
S_y	$= \sum_{i=1}^m [(f_i - f_i^+) / f_i^+]^2 / (m - 1 - p)$ relative standard deviation
t	time
T	dimensionless time ($= kt$)
u_{g1}	phase velocity in absorption column
V	total gas hold-up
\dot{V}	volume flow rate
W	dimensionless duration of start-up period ($= k\tau$)
x_g	fractional content of gas phase in dispersion
y_n	$= (\beta_n / \pi)^2$
β_n	positive roots of $\beta \cotg \beta = -L$
Γ	normalized response of oxygen probe to an exponential concentration change
Γ^1	normalized response of oxygen probe to a unit step change
τ	duration of start-up period ($= V/\dot{V}_g$)

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